The Influence of Substituents on the Optical Rotatory Power of Organic Compounds. The Isomeric Methoxy and Nitro-benzoic Esters of Active Secondary β-Octyl Alcohol.

by

Annie H. Numbers, M.A., B.Sc.

Thesis for the Degree of Ph.D. 1926

CONTENTS.

The relative changes in the rotatory power of a compound produced by the introduction of a number of different substituents have been comparatively little investigated until recent years. Much of the work carried out in this direction has been limited to the study of homologous series, as in the case of the menthyl esters of aliphatic acids examined by Tschugaeff, the corresponding amyl esters by Guye and Chavanne (Comptes rendus 1895, 120, 152) and menthyl esters of carvoxime by Rupe and Wolfsleben (Annalen, 1912, 395, 136).

A great deal of systematic work of this nature has been accomplished by Pickard and Kenyon in connection with optically active secondary carbinols and their esters and ethers.

Two generalisations have emerged from these researches and others of similar type. In the first instance, it is now accepted that the introduction of a methyl group in place of hydrogen often produces a marked change in the rotatory power of the parent compound, but that the subsequent lengthening of the

chain by the introduction of succeeding methylene groups produces less and less change in the rotation, until in many cases a constant value is finally attained.

In the second place, it is frequently observed that the curve representing the change undergone by the molecular rotation in a homologous series as the number of carbon atoms increases is broken by an inflexion corresponding to a maximum or minimum at or about the fifth, tenth and fifteenth carbon atoms in the chain, counting from the asymmetric atom. These effects have been explained by Frankland on the basis of Baeyer's strain theory as being due to the influence of the end of the chain as it returns upon itself in space. Among cases of this kind may be mentioned the carbinols $C_2H_5.CHOH.R$ (Pickard and Kenyon, J.C.S. 1913,1923) and esters of certain secondary carbinols with the fatty acids (Pickard & Kenyon, J.C.S. 1914, 830, 2228, 2262). Many of these ester series exhibit a marked maximum at the valerate and decoate, i.e. at the points where the carbon chain becomes five and ten atoms in length.

A similar effect has been observed by Hilditch (J.C.S., 1909, 95, 1581) among the dimenthyl esters of dicarboxylic acids, the ester of adipic acid having an abnormally high rotation.

Less is known regarding the relative influence of different substituents. In the aliphatic group, the rotatory powers of menthyl esters of halogen-substituted aliphatic acids have been determined by Tschugaeff (J. Russ.Phys.Chem.Soc. 1902, 34,606), Cohen (J.C.S. 1911, 99, 1061) and Hilditch (J.C.S., 1912, 101, 202), from whose work it appears that substitution tends to raise the rotation, and that the relative effect of the three halogens F, Cl, Br is in the inverse order of the atomic weights.

A large number of compounds havebeen prepared by Betti (Gazzetta, 1923, 53, 417) by the condensation of an active base with substituted benzaldehydes, and an examination of their rotatory powers in benzene solution has shown that the influence of substituents on rotation goes hand in hand with their influence on the acidity of the corresponding benzoic acids. A similar substituent effect has

been found in the menthyl esters of monosubstituted acetic acids (Rule & Smith, J.C.S., 1925, 125, 2188).

A detailed examination of the effect of nuclear substitution on the rotation of menthyl benzoate has been carried out by Cohen. In a summary of this work Cohen (J.C.S., 1914, 105, 1895) observes that the rotation of the different o-, m-, and p- substituted esters cannot be explained on the basis of Frankland's lever-arm theory, and concludes that the element or group lying nearest the asymmetric atom produces the greatest effect, which, according to the nature of the group, may be an increase or decrease in rotation value, and that this value approaches the normal for the unsubstituted compound the further the substituent is removed from its proximity to the asymmetric group. The influence of the different o- substituents on the molecular rotation in this case is given by the series

$$NO_2 > COOH > H > I > CH_3 > Br > Cl > F > OCH_3$$

It has recently been pointed out by Rule (J.C.S. 1924, 125, 1122) that those substituents which raise the rotation of menthyl benzoate are m- directive in the influence on benzene substitution, while those

which depress the rotation are o-, p- directive, and that the relative effect of different groups is in agreement with their relative polarity and their relative influence on benzene substitution as we pass from the strongly positive or m- directive nitro group through hydrogen to the strongly negative or o-, p- directive fluoro group.

Further confirmation of the connection between the influence of substituents on rotatory power and on benzene substitution has been obtained by the examination of the menthyl ester of acetophenone o-carboxylic acid. The graded influence of different groups X on the nitration of the benzene derivative C_6H_5X is given by

(A) $NO_2 > COOH > COCH_3 > H > CH_3 > Br > I > Cl > F > (OCH_3?)$

The rotatory power of menthyl acetophenone o-carboxylate places the acetyl group between COOH and hydrogen (Rule & Smith, J.C.S., 1926, 129, 553). The series representing the influence of the groups on rotatory power in this case is therefore

(B) $NO_2 > COOH > COCH_3 > H > I > CH_3 > Br > Cl > F > OCH_3$

in which the agreement with A above is broken only by a slight displacement of the iodine atom. Substituents in the m- and p- positions produce little

or no change in the rotation of menthyl benzoate.

It has been found that the esters of the cyclic alcohol, menthol, behave in a remarkably regular manner when examined from the standpoint of optical activity, most of them exhibiting normal and apparently simple dispersion, and undergoing little change in rotatory power with alteration of solvent and temperature. It was therefore thought of interest to investigate the influence of substituents on certain esters of secondary β-octyl alcohol, since these compounds generally exhibit complex dispersion and are known to be much more sensitive to alterations in external conditions (Pickard & Kenyon, J.C.S., 1914, 105, 837; Hunter, J.C.S., 1924, 125, 1389). The following pages contain the results of an examination of the active octyl esters of o-, m-, and p- substituted methoxy and nitro benzoic acids. The rotatory powers of the compounds in the homogeneous state were determined at temperatures between 20° and 95°C. and in the case of the methoxy esters for light of the D line, and the yellow, green and violet mercury lines. Owing to the yellow colour of the nitro-esters the violet mercury line could not

be employed, but rotations for all four wave lengths were obtained using 5% alcoholic solutions of the esters. The rotatory powers of these esters are compared with those of octyl benzoate, octyl hydrogen phthalate (Pickard & Kenyon) and the octyl chloro-benzoates.*

* Unpublished work by H. G. Rule and T. R. Paterson, which Dr Paterson left unfinished and which I have now completed.

EXPERIMENTAL.

The active β-octyl alcohol required for this investigation was obtained by resolving the racemic alcohol after the manner described by Pickard and Kenyon (J.C.S. 1907, 2058) and modified later by Kenyon (J.C.S. 1922, 2540). Phthalic anhydride and the inactive alcohol were heated together for about twenty five hours at 120°C. It was found that a better yield of octyl hydrogen phthalate was obtained if the heating was carried on longer than for the fifteen hours prescribed in the above paper. Excess of ethyl alcohol was added and the whole heated for some time on the water bath. The bulk of the ethyl alcohol was then distilled off and the contents of the flask added to sodium carbonate solution. The solution of sodium octyl phthalate so formed was extracted three times with petroleum ether to remove traces of neutral esters, unchanged alcohol and ketonic impurities. It was found most important to extract completely at this stage, as the presence of unchanged octyl alcohol hindered the crystallisation of β-octyl hydrogen phthalate at a later stage. The alkaline aqueous solution was acidified and ex-

tracted with ether. After drying the ethereal solution over sodium sulphate, the ether was distilled off, and the last traces of water and unchanged octyl alcohol were removed by distillation under diminished pressure. The inactive β-octyl hydrogen phthalate thus obtained was recrystallised twice from petroleum ether, the amount of petroleum ether required for each crystallisation being approximately 1 c.c. of solvent for each gramme of the ester used.

The purified β-octyl hydrogen phthalate was dissolved in warm acetone, to which the calculated amount of anhydrous brucine was then added, and the mixture heated until solution was complete. On cooling, crystals of the brucine salt of d-octyl phthalate separated from the liquid, while the salt of the laevo compound remained in solution. The crystals were filtered and washed with acetone. The filtrate containing the laevo enantiomorph was poured into dilute hydrochloric acid, when the l-octyl hydrogen phthalate separated as an oil which quickly crystallised. This was filtered, washed and dried. The crystals of the dextro compound were dissolved in a minimum of hot ethyl alcohol and

poured into dilute hydrochloric acid.

The two lots of partly active β-octyl hydrogen phthalate so obtained were separately crystallised twice from 90% acetic acid. It was found that the use of an equal weight of solvent for a given weight of ester gave the most satisfactory results. The phthalates were recrystallised until the rotations reached the value quoted by Pickard and Kenyon (loc. cit.) $[\alpha]_D = \pm 48{\cdot}2^\circ$ (in 5% alcoholic solution).

β-Octyl hydrogen phthalate was converted into the alcohol by treating one molecular part with two and a half molecular parts of potassium hydroxide dissolved in a minimum of water. The mixture was heated under reflux for four hours, after which the free alcohol was extracted with ether and the ethereal solution dried over sodium sulphate. Finally the ether was distilled off and the alcohol fractionated (b.p. $83^\circ/20$ mm.).

In a one decimetre tube the d-alcohol employed had a rotation of $[\alpha]_D^{14^\circ} = +8{\cdot}14^\circ$ and the laevo alcohol $[\alpha]_D^{16^\circ} = -8{\cdot}12^\circ$ and $-8{\cdot}14^\circ$ (two preparations).

Preparation of 1-β-octyl o-methoxy benzoate.

1 - β-Octyl o-methoxy benzoate was prepared from pure o-cresol in the following steps:-

$$HO.C_6H_4.CH_3 \xrightarrow{(CH_3)_2SO_4+NaOH} CH_3O.C_6H_4.CH_3$$

$$CH_3O.C_6H_4.CH_3 \xrightarrow{K\,Mn\,O_4} CH_3O.C_6H_4.COOH$$

$$CH_3O.C_6H_4.COOH \xrightarrow{P\,Cl_5} CH_3O.C_6H_4.COCl.$$

$$CH_3O.C_6H_4.COCl \xrightarrow{\text{octyl alcohol}} CH_3O.C_6H_4.COOC_8H_{17}.$$

(1). o-Tolyl methyl ether was prepared from o-cresol by methylating it with dimethyl sulphate in the presence of sodium hydroxide. The o-cresol (100 gm) and solid sodium hydroxide (18 gm.) were dissolved in 130 gm. of water and shaken for fifteen minutes with 51 gm. of dimethyl sulphate. A further quantity of sodium hydroxide (18·6 gm. in 120 cc. water) was then added, and the whole was boiled under reflux for seven hours. An oil separated out which was removed in a separating funnel, washed several times with sodium hydroxide and subsequently with water. It was dried over sodium sulphate and purified by distillation.

(2) o-Methoxy benzoic acid.

A weighed quantity of o-tolyl methyl ether was poured into a flask containing water. The flask was fitted with a stirrer and from time to time small quantities of solid potassium permanganate were added until the amount required to oxidise the weight of ether taken had been used. The mixture was kept at a temperature of 40°C. It was found that a higher temperature led to decomposition of the acid and a poor yield. The acid was purified by repeated crystallisation from water, the final product melting at 99·5°C. Bromwell quotes 98·5° - 99° (Ann. 19, 1897, 577).

(3). o-Methoxy benzoyl chloride.

o-Methoxy benzoyl chloride was prepared by treating dry o-methoxy benzoic acid with phosphorus pentachloride in a small flask under reflux. The mixture was warmed until the reaction started, and after the first vigorous evolution of HCl gas had ceased, it was heated for an hour on an oil bath. After removing the phosphorus oxychloride under

reduced pressure in a current of dry air, the acid chloride was fractionated. It is most important that the o-methoxy benzoic acid be pure and free from salicylic acid. Even a small quantity of the latter acid leads to complete decomposition on treatment with phosphorus pentachloride. The o-methoxy benzoyl chloride used boiled at 131 - 132° under 12 m.m. pressure. . Pinnow and Müller quote 254° at 760 m.m. (B. 28, 1895, 158).

(4). 1-β-Octyl o-methoxy benzoate.

A weighed quantity of o-methoxy benzoyl chloride (12·5 gm.) was treated with the theoretical amount of 1-β-octyl alcohol (9·5 gm.) and just over two molecular parts of pyridine (12 gm.). The whole was heated under reflux for four hours in an oil bath at 120°C. The cold mixture was diluted with four to five times its volume of water and the ester extracted twice with ether. The ethereal layer was washed with dilute hydrochloric acid, followed by diluted sodium hydroxide solution and finally with water to remove alkali. It was dried over calcium chloride

and after distilling off the ether and any unchanged β-octyl alcohol, the ester was fractionated twice under diminished pressure.

l-β-Octyl o-methoxy benzoate was obtained as a colourless, odourless liquid with a boiling point of 187·5° under 13 m.m. pressure. Yield - 12 gm.

The rotation of the ester was measured at 20°C. after the second fractionation. The value of the rotation was unchanged on being measured after another fractionation.

Analysis.

·1979 gm. ester gave H = 9·16%, C = 72·61%.

$C_{16}H_{24}O_3$ requires H = 9·15%, C = 72·68%.

Density Determinations:

The density of l-β-octyl o-methoxy benzoate was measured at four different temperatures between 20° and 85°, using a pyknometer with a capacity of about 3 c.c. The values of the densities at these temperatures were calculated with reference to that of water at 4° C.

t°	$20{\cdot}3^{\circ}$	$42{\cdot}4^{\circ}$	$57{\cdot}9^{\circ}$	$81{\cdot}35^{\circ}$
d_4^t	1·0004	0·9824	0·9699	0·9513

A graph - which proved to be a straight line - was made by plotting the density against the corresponding temperature, and from this the values of the density at 20°, 40°, 60°, 80°, 90°C. were read off. These values are used in the calculation of molecular rotations given on p. /8 .

In the following pages are given tables recording (1) the experimental values of rotations found at the four temperatures used, and, in addition, the calculated values for rotations assuming that their variation from one wave length to another is governed by a Drude one term equation; (2) the value of the rotations at 20°,40°,60°,80° and 90° obtained from a graph of the rotation against temperature, together with the specific rotations, and (3) the molecular rotations calculated from these values. Following these tables is a graph showing the results of plotting the reciprocal of the rotation of the homogeneous o-methoxy ester against the square of the wave length.

l-β-Octyl o-methoxy benzoate.

Temp.	Length of observation tube in mm.	Rotations α	$\frac{\alpha_{gr}}{\alpha_D}$	Drude Equation (one term) K	Drude Equation (one term) λ_o^2	Drude Equation (one term) α(calculated)	Difference α(obs) - α(calc).
24·4°	50	α_D = 6·48 α_{ye} = 6·60 α_{gr} = 7·32 α_{vi} = 10·01	1·130	2·892	-·0990	α_D = 6·48 α_{ye} = 6·68 α_{gr} = 7·28 α_{vi} = 10·01	± ·00 - ·08 + ·04 ± ·00
39·6°	50	α_D = 6·94 α_{ye} = 7·14 α_{gr} = 7·95 α_{vi} = 11·45	1·145	2·773	-·0523	α_D = 6·94 α_{ye} = 7·18 α_{gr} = 7·91 α_{vi} = 11·45	± ·00 - ·04 + ·04 ± ·00
55°	50	α_D = 7·38 α_{ye} = 7·67 α_{gr} = 8·58 α_{vi} = 12·95	1·163	2·701	-·0186	α_D = 7·38 α_{ye} = 7·66 α_{gr} = 8·53 α_{vi} = 12·95	± ·00 + ·01 + ·05 ± ·00
92·1°	50	α_D = 8·14 α_{ye} = 8·49 α_{gr} = 9·51 α_{vi} = 15·48	1·168	2·702	+·0153	α_D = 8·14 α_{ye} = 8·48 α_{gr} = 9·55 α_{vi} = 15·47	± ·00 + ·01 - ·04 + ·01

l - β - Octyl o - methoxy benzoate.

Table showing densities, rotations and specific rotations.

Temp.	Density	α_D	α_{ye}	α_{gr}	α_{vi}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[\alpha]_{vi}$
20°	1·0006	6·30	6·47	7·12	9·53	12·59	12·93	14·23	19·05
40°	0·9844	6·95	7·18	8·00	11·55	14·12	14·59	16·25	23·47
60°	0·9683	7·48	7·78	8·70	13·24	15·45	16·07	17·97	27·35
80°	0·9523	7·93	8·27	9·26	14·69	16·66	17·37	19·45	30·85
90°	0·9443	8·11	8·47	9·48	15·37	17·18	17·94	20·08	32·55

For molecular rotations see next page.

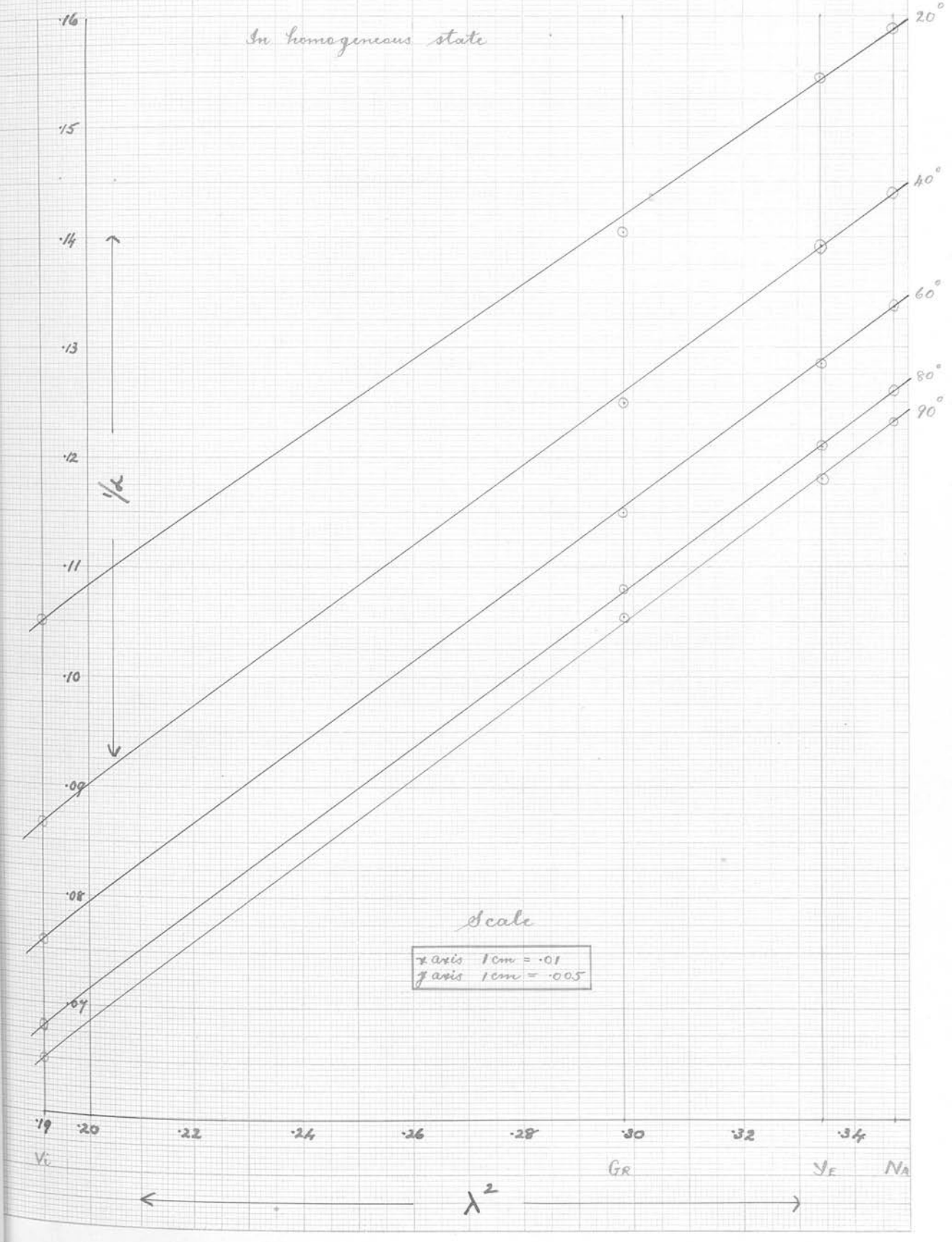
l - β - octyl o - methoxy benzoate.

Table showing molecular rotations (calculated from specific rotations tabulated on previous page.)

Temp.	$[M]_D$	$[M]_{ye}$	$[M]_{gr}$	$[M]_{vi}$
20°	33·27	34·17	37·60	50·33
40°	37·31	38·54	42·94	62·00
60°	40·82	42·46	47·48	72·25
80°	44·00	45·89	51·38	81·51
90°	45·38	47·39	53·05	86·00

l-β-6ctyl o-methoxy benzoate

Graph showing $1/\alpha$ against λ^2.



Preparation of l-β-octyl m-methoxy benzoate.

This ester was prepared from m-cresol in the following stages:-

(1) $HO.C_6H_4.CH_3 \xrightarrow{(CH_3)_2SO_4 + NaOH} CH_3O.C_6H_4.CH_3$

(2) $CH_3O.C_6H_4.CH_3 \xrightarrow{K\ MnO_4} CH_3O.C_6H_4.COOH$

(3) $CH_3O.C_6H_4.COOH \xrightarrow{P\ Cl_5} CH_3O.C_6H_4.COCl$

(4) $CH_3O.C_6H_4.COCl \xrightarrow{octyl\ alcohol} CH_3O.C_6H_4.COOC_8H_{17}$

(1) m-Cresol and solid sodium hydroxide were dissolved in water and shaken for fifteen minutes with dimethyl sulphate. The preparation was then continued as for o-methyl tolyl ether.
The boiling point was 178° C.
Pinette gives 177·2°C. (Ann. 243, 1888, 41).

(2). m-Tolyl methyl ether was converted into the corresponding methoxy benzoic acid by the method of Oppenheim and Pfaff (B. 1875, 8, 887). The tolyl ether was added to the theoretical amount of potassium permanganate contained in dilute (2½ per cent) aqueous solution, and the oxidation allowed to proceed at the ordinary temperature. The mixture was kept well stirred until the oil floating on the surface had disappeared. In about two weeks 120 gm. of the ether were oxidised. It was found that the best yield was obtained if these conditions were strictly observed. Any increase in the concentration of the permanganate or any application of heat to the mixture led to a diminution in the yield of acid. The solution was decolorised with sulphur dioxide gas, extracted twice with ether, and the ethereal extract shaken with sodium hydroxide to remove the carboxylic acid. Any unchanged m-tolyl ether remained in the ether. The aqueous solution was treated with concentrated hydrochloric acid to precipitate the m-methoxy benzoic acid. The latter was filtered off and purified by repeated crystallisation from ligroin. The pure product melted sharp-

ly at 105·8°C. Oppenheim and Pfaff (loc.cit) quote 106° C.

(3). m-Methoxy benzoyl chloride was prepared from m-methoxy benzoic acid by the use of phosphorus pentachloride, in the same way as o-methoxy benzoyl chloride was prepared from o-methoxy benzoic acid. The phosphorus oxychloride was removed under reduced pressure in a current of dry air and the acid chloride fractionated. The boiling point was 116°C. under 11·5 mm. Ullmann and Goldberg give 242 - 243°/733 mm. (B. 35, 1902, 2813).

(4). 1-β-octyl m-methoxy benzoate.

The method and quantities were the same as those adopted for the preparation of 1-β-octyl o-methoxy benzoate, using however, m-methoxy benzoyl chloride in place of the o-methoxy derivative.

1-β-octyl m-methoxy benzoate was obtained as a colourless, odourless liquid boiling at 187·5°C under 12 mm. pressure. Yield - 13 gm. It was fractionated twice and its rotation measured. Another distillation produced no difference in the rotatory power of the compound.

Analysis.

·2088 gm. gave H = 9·27%, C = 72·60%

$C_{16} H_{24} O_5$ requires H = 9·15%, C = 72·68%.

Density Determinations:

The density of the compound was measured at four temperatures using a calibrated pyknometer using 3 ccs. The values were calculated as before with reference to water at 4° C.

t	20·42°	41·6°	58·2°	80·45°
d_4^t	0·9939	0·9771	0·9641	0·9464

As before the values of the density at 20°, 40°, 60°, 80° and 90° C. were obtained from the graph of density plotted against temperature.

On the following four pages are given the values of rotatory powers and the graph of the reciprocal of the rotation plotted against the square of the wave length.

1 - β - Octyl m - methoxy benzoate.

Temperature	Length of observation tube in mm.	Rotations α	$\frac{\alpha_{gr}}{\alpha_D}$	Drude Equation (one term) K	λ_o^2	α(calculated)	Difference α (obs) - α (calc)
20·4°	50	α_D = 17·63 α_{ye} = 18·43 α_{gr} = 21·04 α_{vi} = 36·76	1·193	5·332	·0448	α_D = 17·63 α_{ye} = 18·43 α_{gr} = 21·04 α_{vi} = 36·76	± ·00 ± ·00 ± ·00 ± ·00
37·1°	50	α_D = 17·24 α_{ye} = 18·03 α_{gr} = 20·62 α_{vi} = 36·05	1·196	5·200	·0457	α_D = 17·24 α_{ye} = 18·03 α_{gr} = 20·59 α_{vi} = 36·06	± ·00 ± ·00 + ·03 - ·01
68·5°	50	α_D = 16·44 α_{ye} = 17·17 α_{gr} = 19·64 α_{vi} = 34·52	1·195	4·941	·0468	α_D = 16·44 α_{ye} = 17·19 α_{gr} = 19·65 α_{vi} = 34·53	± ·00 - ·02 - ·01 - ·01
92·9°	50	α_D = 15·90 α_{ye} = 16·59 α_{gr} = 19·02 α_{vi} = 33·33	1·196	4·785	·0464	α_D = 15·90 α_{ye} = 16·63 α_{gr} = 19·00 α_{vi} = 33·35	± ·00 - ·04 + ·02 - ·02

l - β - Octyl m - methoxy benzoate.

Table showing densities, rotations and specific rotations.

Temp.	Density	α_D	α_{ye}	α_{gr}	α_{vi}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[\alpha]_{vi}$
20°	0·9945	17·64	18·44	21·05	36·78	35·48	37·08	42·33	73·97
40°	0·9785	17·18	17·93	20·50	35·85	35·12	36·65	41·90	73·27
60°	0·9627	16·69	17·42	19·93	34·90	34·67	36·19	41·40	72·50
80°	0·9467	16·20	16·90	19·38	33·97	34·23	35·70	40·94	71·77
90°	0·9389	15·96	16·65	19·09	33·48	34·00	35·47	40·67	71·32

For table showing molecular rotations see next page.

1 - β - Octyl m - methoxy benzoate.

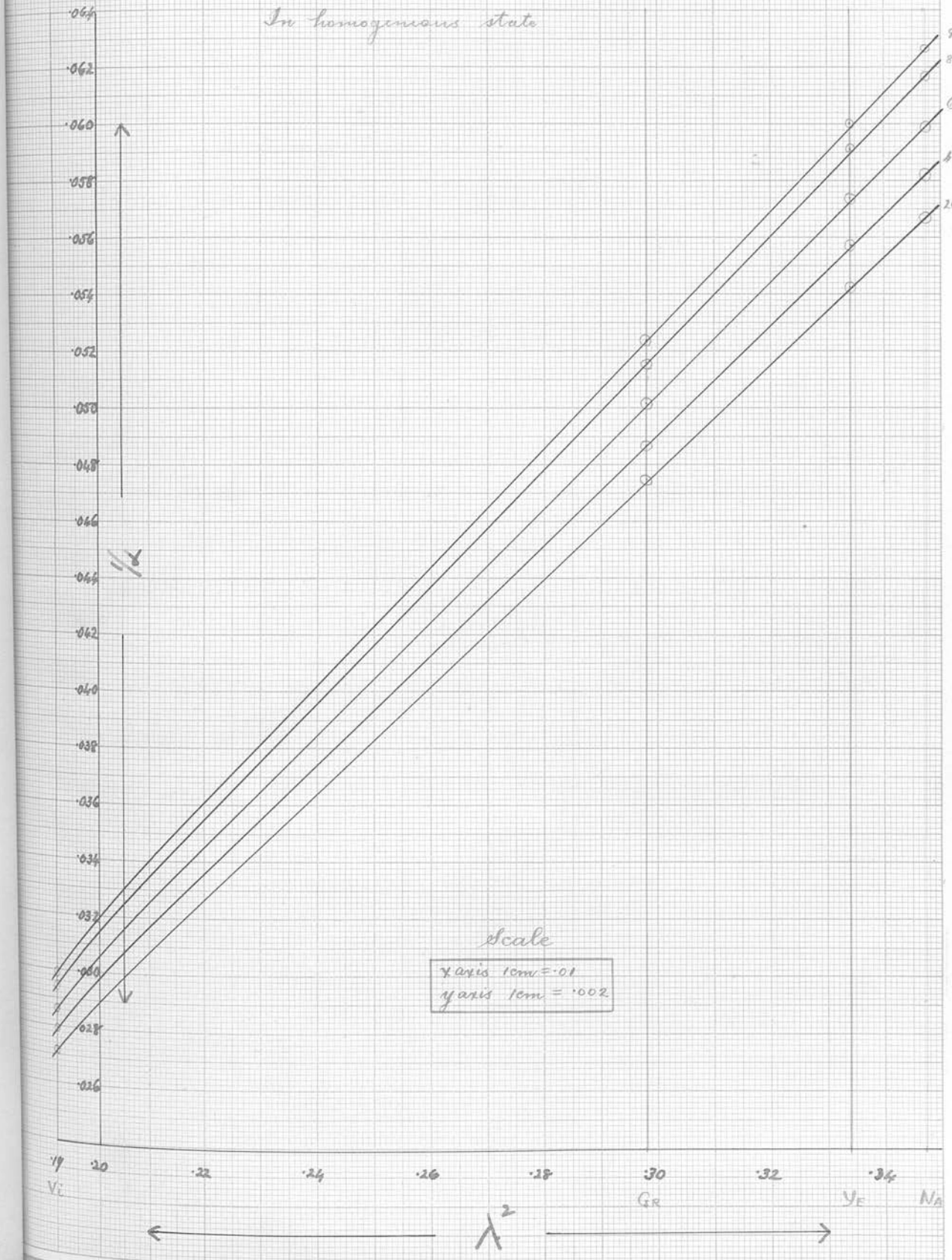
Table showing molecular rotations (calculated from specific rotations tabulated on previous page.)

Temp.	$[M]_D$	$[M]_{ye}$	$[M]_{gr}$	$[M]_{vi}$
20°	93·73	97·98	111·8	195·4
40°	92·77	96·82	110·7	193·6
60°	91·61	95·61	109·4	191·6
80°	90·42	94·33	108·2	189·6
90°	89·82	93·70	107·4	188·4

l-β-Octyl m-methoxy benzoate

Graph showing $1/\alpha$ against λ^2.

In homogeneous state



Preparation of l-β-octyl p-methoxy benzoate.

This ester was prepared from anisaldehyde in the following stages:-

(1) $C_6H_4(OCH_3)CHO \xrightarrow{K\,MnO_4} C_6H_4(OCH_3)COOH$

(2) $C_6H_4(OCH_3)COOH \xrightarrow{PCl_5} C_6H_4(OCH_3)COCl$

(3) $C_6H_4(OCH_3)COCl \xrightarrow{\text{octyl alcohol}} C_6H_4(OCH_3)COOC_8H_{17}$

(1). Anisic Acid

Anisic acid was prepared by warming a weighed quantity of anisaldehyde with a small quantity of 5% potassium permanganate solution. From time to time small quantities of the potassium permanganate were added until the calculated amount required for the oxidisation of the aldehyde had been added. After the reaction was complete, the solution was decolorised by passing sulphur dioxide gas through it. Anisic acid separated out and was filtered off at the pump. It was purified by repeated crystallisation from water. The final product melted at 184°C. Oppenheim and Pfaff quote 184·2° in Ber. 8. 893.

(2) Anisoyl Chloride.

The anisic acid was carefully dried in vacuo and converted into the acid chloride by warming with one molecular equivalent of phosphorus pentachloride. Phosphorus oxychloride was removed by distillation under reduced pressure, the air passing through the capillary being dried by means of calcium chloride. The anisoyl chloride was then distilled in vacuo, using an air bath. It boiled at 150°C/30 mm. and solidified in the receiver. Cahours quotes 262° at ordinary pressure (Ann. 70, 47).

(3) l-β-octyl p-methoxy benzoate.

A weighed quantity of anisoyl chloride (12·5 gm) was treated with the theoretical amount of l-octyl alcohol (9·5 gm) and then with a little over two molecular parts of pyridine (12·5 gm). The whole was heated under reflux for four hours in an oil bath at 120° C. The cold mixture was diluted with four to five times its volume of water and the ester extracted twice with ether. The ethereal layer was washed with dilute hydrochloric acid, followed by diluted sodium hydroxide solution and finally with water to remove

alkali. It was then dried over calcium chloride. After distilling off the ether and any unchanged β-octyl alcohol the ester was fractionated under diminished pressure.

l-β-octyl p-methoxy benzoate was obtained as a colourless, odourless liquid boiling at 189°C. under 13 mm. pressure. Yield - 14 gm.

The rotation of the ester was measured at a definite temperature (20° C. approximately) and the compound was then again fractionated, rejecting three to four cubic centimetres. The value of the rotation was not changed by this second distillation.

Analysis.

·1993 gm. ester gave H = 9·19%, C = 72·52%.

$C_{16}H_{24}O_3$ requires H = 9·15%, C = 72·68%.

Density Determinations:

The density of this ester was determined at four temperatures, use being made of a carefully calibrated pyknometer holding about 3 c.cs. The

values were calculated with reference to that of water at 4° C.

t°	23·9°	41°	57·9°	81·8°
d_4^t	0·9940	0·9807	0·9677	0·9488

The above densities, on being plotted against the corresponding temperatures, gave a straight line, from which the values of the densities at 20°, 40°, 60°, 80° and 90° C. were read off. These values are used in the calculation of molecular rotations, which are tabulated on p. 34.

On the following four pages will be found tables and a graph compiled as for the previous esters.

1 - β - Octyl p - methoxy benzoate.

Temperature	Length of observation tube in mm.	Rotations α	$\frac{\alpha_{gr}}{\alpha_D}$	Drude Equation (one term) K	Drude Equation (one term) λ_o^2	Drude Equation (one term) α(calculated)	Differences α (obs) - α (calc)
21·5°	50	α_D = 21·33 α_{ye} = 22·33 α_{gr} = 25·56 α_{vi} = 45·81	1·198	6·283	·0527	α_D = 21·33 α_{ye} = 22·33 α_{gr} = 25·59 α_{vi} = 45·80	± ·00 ± ·00 - ·03 + ·01
39°	50	α_D = 20·87 α_{ye} = 21·88 α_{gr} = 25·05 α_{vi} = 44·80	1·200	6·150	·0526	α_D = 20·87 α_{ye} = 21·85 α_{gr} = 25·04 α_{vi} = 44·80	± ·00 + ·03 + ·01 ± ·00
65·4°	50	α_D = 20·22 α_{ye} = 21·08 α_{gr} = 24·16 α_{vi} = 43·26	1·195	5·977	·0517	α_D = 20·22 α_{ye} = 21·17 α_{gr} = 24·25 α_{vi} = 43·25	± ·00 - ·09 - ·09 + ·01
93·7°	50	α_D = 19·42 α_{ye} = 20·23 α_{gr} = 23·21 α_{vi} = 41·75	1·195	5·715	·0530	α_D = 19·42 α_{ye} = 20·33 α_{gr} = 23·30 α_{vi} = 41·76	± ·00 - ·10 - ·09 - ·01

l - β - Octyl p - methoxy benzoate.

Table showing densities, rotations and specific rotations.

Temp.	Density	α_D	α_{ye}	α_{gr}	α_{vi}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[\alpha]_{vi}$
20°	0·9968	21·37	22·38	25·61	45·89	42·88	44·90	51·38	92·07
40°	0·9814	20·84	21·80	24·97	44·78	42·47	44·43	50·89	91·26
60°	0·9661	20·30	21·22	24·30	43·65	42·03	43·93	50·31	90·36
80°	0·9503	19·78	20·64	23·68	42·52	41·63	43·44	49·84	89·49
90°	0·9427	19·51	20·36	23·34	41·96	41·39	43·20	49·52	89·02

For molecular rotations see next page.

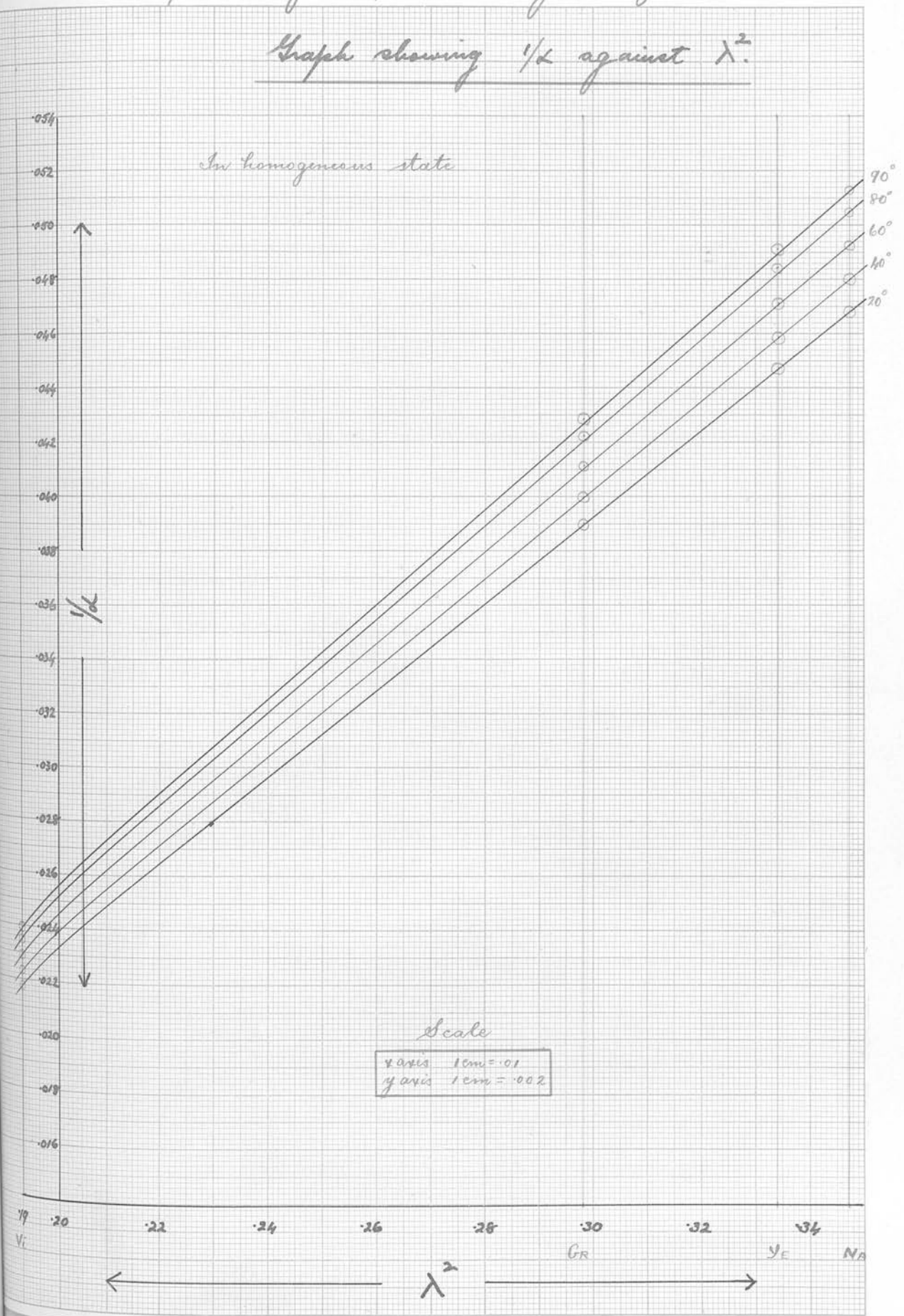
l - β - Octyl p - methoxy benzoate.

Table showing molecular rotations (calculated from specific rotations tabulated on previous page).

Temp.	$[M]_D$	$[M]_{ye}$	$[M]_{gr}$	$[M]_{vi}$
20°	113·3	118·6	135·8	243·3
40°	112·2	117·4	134·4	241·1
60°	111·0	116·1	132·9	238·7
80°	110·0	114·8	131·7	236·4
90°	109·4	114·1	130·8	235·2

l-β- Octyl p-methoxy benzoate.

Graph showing $1/\alpha$ against λ^2.



Preparation of l-β-Octyl o-nitro-benzoate.

The ester was prepared from o-nitro benzoyl chloride (Kahlbaum) and l-β-octyl alcohol. The o-nitro benzoyl chloride was fractionated under reduced pressure, the substance employed boiling at 148° under 9 mm. pressure. The octyl ester was prepared in the usual way, starting from 10 gm. of the alcohol, 14·2 gm. of the acid chloride and 12 gm. of pyridine, and was purified in the same manner as the o-methoxy benzoate (see p. 13).

l-β-Octyl o-nitro-benzoate was obtained as a pale yellow odourless liquid with a boiling point of 204° C. under 15 m.m. pressure. Yield - 14 gm. It was twice fractionated and the rotatory power remained constant after the second distillation.

Analysis.

0·2162 gm. gave H = 7·76%, C = 64·47%.

0·2699 gm. gave N = 5·24%.

$C_{15}H_{21}NO_4$ requires H = 7·58%, C = 64·48%, N = 5·02%.

Density Determinations.

The density of the ester was measured at four temperatures as in the case of the methoxy esters previously described and the values at 20°, 40°, 60°, 80° and 90° were read off from the graph so obtained. The table showing the latter values is given on p. 40.

t	24·2°	41·8°	61·1°	82·5°
d_4^t	1·0701	1·0560	1·0407	1·0234

On the following pages will be found tables giving densities and rotatory powers of the o-nitrobenzoic ester, together with a graph showing the values of $1/\alpha$ plotted against λ^2 for the compound in the homogeneous state and in 5% alcoholic solution.

l - β - octyl o - nitro benzoate

Temperature	Length of observation tube in mm.	Rotations α_D	Rotations α_{ye}	Rotations α_{gr}	α_{gr}/α_D
23·5°	50	23·26	24·54	28·88	1·241
38·3	50	22·70	23·90	28·07	1·236
65°	50	21·77	22·96	26·92	1·237
92·2°	50	20·98	21·97	25·90	1·235

α_{vi} could not be determined on account of yellow colour of liquid.

1-β-Octyl o-nitro benzoate in alcoholic solution (approx. 5%).

Solvent.	gm. of ester in 100 cc. of solvent.	Temp.	Length of observation tube.	Rotations.	α_{gr}/α_D	[α] Specific Rotations	[M] Molecular Rotations
Alcohol	5·0900	20·8°C	50 m.m.	α_D = 1·42 α_{ye} = 1·69 α_{gr} = 1·90 α_{vi} = 3·83	1·338	55·80 66·40 74·65 150·5	155·8 185·4 208·4 420·2

Drude Equation applied to the above rotations.

Rotations.	Drude Equation (one term) K	λ_o^2	α (calc)	Differences α(obs) - α (calc)
α_D = 1·42 α_{ye} = 1·69 α_{gr} = 1·90 α_{vi} = 3·83	3·553	·0971	α_D = 1·42 α_{ye} = 1·50 α_{gr} = 1·77 α_{vi} = 3·83	± ·00 + ·19 + ·13 ± ·00

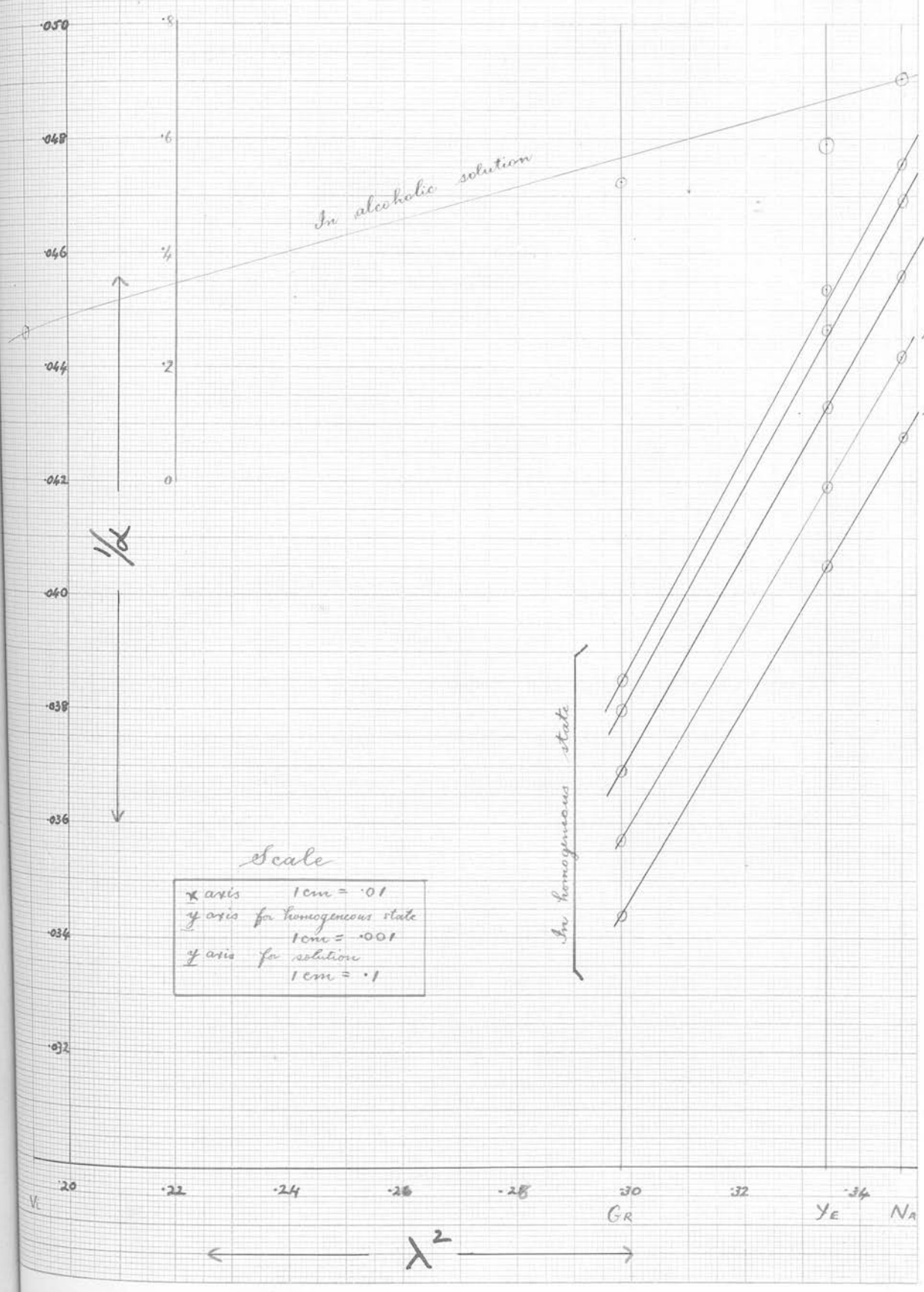
l - β - Octyl o - nitro benzoate.

Table showing densities, rotations, specific rotations and molecular rotations.

Temp.	Density	α_D	α_{ye}	α_{gr}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[M]_D$	$[M]_{ye}$	$[M]_{gr}$
20°	1·0735	23·38	24·69	29·08	43·56	46·00	54·18	121·6	128·4	151·3
40°	1·0571	22·63	23·86	28·00	42·82	45·15	52·97	119·6	126·1	147·9
60°	1·0410	21·94	23·10	27·08	42·15	44·38	52·03	117·6	123·9	145·3
80°	1·0251	21·32	22·39	26·31	41·60	43·68	51·33	116·1	122·0	143·3
90°	1·0172	21·03	22·04	25·98	41·35	43·33	51·08	115·4	121·0	142·6

l-β-Octyl o-nitro benzoate.

Graph showing 1/α against λ^2.



Scale

x axis	1 cm = ·01
y axis for homogeneous state	1 cm = ·001
y axis for solution	1 cm = ·1

Preparation of d-β-Octyl m-nitro benzoate.

d-β-Octyl m-nitro benzoate was prepared from purified m-nitro benzaldehyde as follows:-

$NO_2 . C_6H_4 . CHO \xrightarrow{K\ MnO_4} NO_2 . C_6H_4 . COOH$

$NO_2 . C_6H_4 . COOH \xrightarrow{PCl_5} NO_2 . C_6H_4 . COCl$

$NO_2 . C_6H_4 . COCl \xrightarrow{\text{octyl alcohol}} NO_2 . C_6H_4 . COOC_8H_{17}$.

(1) m-Nitro benzoic acid.

This was prepared from m-nitro benzaldehyde by oxidising with a 5% solution of potassium permanganate in the usual way. After no more of the solution was decolorised on heating, dilute sulphuric acid was added until the mixture was acid. It was then decolorised with gaseous sulphur dioxide and made alkaline. Any unchanged aldehyde having been extracted with ether, the acid was precipitated with concentrated hydrochloric acid, filtered and dried. The acid was purified by repeated crystallisations from water until it melted at 140 - 141° C.

(2) m-Nitro benzoyl chloride.

The acid chloride was prepared by warming the free dried acid with an equivalent amount of phos-

phorus pentachloride until evolution of hydrochloric acid gas ceased. The phosphorus oxychloride was distilled off under reduced pressure and the m-nitro benzoyl chloride fractionated. It boiled at 156° - 158° under 20 m.m. pressure. It is quoted at 275°-278° under ordinary pressure (Hugh, Ber. 7, 1267) and 183 - 184° under 50 - 55 m.m. (Claisen and Thompson, Ber. 12, 1943).

(3) d-β-Octyl m-nitro benzoate.

The method and quantities employed for making this ester were the same as those used for the preparation of the o-ester. The final product on fractionation boiled at 211·9°C. under 18 m.m., and was a pale yellow odourless liquid. Yield - 13·5 gm. The rotation remained unchanged after two fractionations.

Analysis.

·2074 gm. ester gave H = 7·63%, C = 64·62%.

·2975 gm. ester gave N = 5·26%.

$C_{15}H_{21}NO_4$ requires H = 7·58%, C = 64·48%, N = 5·02%.

Density Determinations:

The density of the ester was measured at four temperatures and the values at 20°, 40°, 60°, 80°, and 90° were determined from the graph of density against the corresponding temperature. These are used for calculations given on p.47.

t	24·1°	41°	57·4°	83·8°
d_4^t	1·0725	1·0587	1·0453	1·0238

On the following pages are shown tables giving densities and rotations of the m-nitro benzoic ester, and the graph of $1/\alpha$ against λ^2 for the compound in the homogeneous state and in 5% alcoholic solution.

d - β - octyl m - nitro benzoate.

Temperature	Length of observation tube in mm.	Rotations α_D	Rotations α_{ye}	Rotations α_{gr}	α_{gr}/α_D
20·0°	50	20·77	21·68	24·38	1·198
39·0°	50	19·81	20·76	23·63	1·193
55·7°	50	19·07	20·00	22·79	1·195
94·0°	50	17·53	18·40	21·01	1·198

α_{vi} could not be determined on account of yellow colour of liquid.

d-β-Octyl m-nitro benzoate in alcoholic solution (approx.5%)

Solvent.	gm.of ester in 100 cc. of solvent.	Temp.	Length of observation tube.	Rotations	α_{gr}/α_D	[α] Specific Rotations	[M] Molecular Rotations
Alcohol	5·1436	20·2°C	2 dcm.	α_D = 3·80 α_{ye} = 3·99 α_{gr} = 4·51 α_{vi} = 7·78	1·187	36·94 38·79 43·84 75·63	103·1 108·3 122·4 211·2

Drude Equation applied to the above rotations.

Rotations.	Drude Equation (one term) K	λ_o^2	α (calc)	Differences α(obs) - α (calc)
α_D = 3·80 α_{ye} = 3·99 α_{gr} = 4·51 α_{vi} = 7·78	1·169	0·0396	α_D = 3·80 α_{ye} = 3·97 α_{gr} = 4·52 α_{vi} = 7·78	± ·00 + ·02 - ·01 ± ·00

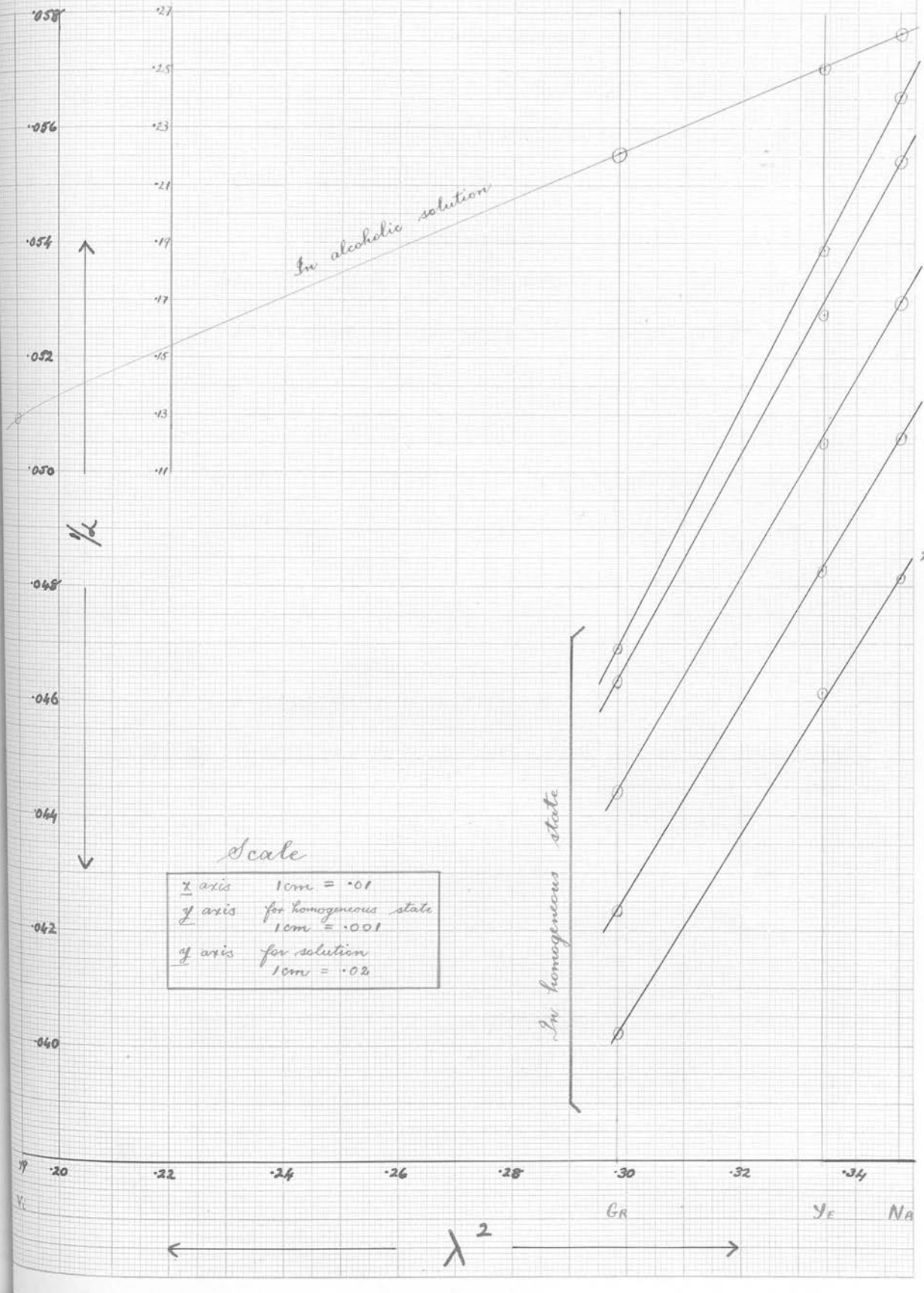
d - β - octyl m - nitro benzoate.

Table showing densities, rotations, specific rotations and molecular rotations.

Temp.	Density	α_D	α_{ye}	α_{gr}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[M]_D$	$[M]_{ye}$	$[M]_{gr}$
20°	1·0758	20·77	21·68	24·88	38·61	40·31	46·25	107·8	112·5	129·1
40°	1·0594	19·77	20·72	23·62	37·32	39·12	44·59	104·2	109·2	124·5
60°	1·0430	18·87	19·80	22·51	36·18	37·97	43·17	101·0	106·0	120·5
80°	1·0266	18·06	18·95	21·57	35·18	36·92	42·02	98·23	103·1	117·3
90°	1·0185	17·69	18·56	21·15	34·74	36·45	41·53	96·99	101·8	116·0

d-β-6ctyl m-nitro benzoate.

Graph showing 1/d against λ^2



Preparation of d-β-Octyl p-nitro benzoate.

d-β-Octyl p-nitro benzoate was prepared from refractionated p-nitro benzoyl chloride supplied by Kahlbaum. The method and quantities employed in this case were the same as those for octyl o-nitro benzoate. After the ether and unchanged alcohol had been removed from the dry ester, the contents of the flask were allowed to cool, when they set to a pale yellow solid. Yield - 16 gm. This was recrystallised from ethyl alcohol until the rotation remained constant. The solid had a melting point of 29·5 - 30° C.

Analysis.

Found C = 64·47%, H = 7·72%, N = 5·29%.

$C_{15}H_{21}NO_4$ requires C = 64·48%, H = 7·58%, N = 5·02%.

Density Determinations.

The density was measured at four temperatures as in the case of each of the other esters and a density temperature curve drawn from which the values at 30°, 40°, 60°, 80° and 90° were read off.

t	32·9°	52·75°	63·25°	80·1°
d_4^t	1·0631	1·0471	1·0384	1·0248

On the following pages are given tables showing densities and rotations of the p-nitro benzoic ester, and the graph of $1/\alpha$ against λ^2 for the compound in the homogeneous state and in 5% alcoholic solution.

d - β - Octyl p - nitro benzoate.

Temperature	Length of observation tube in mm.	Rotations			α_{gr}/α_D
		α_D	α_{ye}	α_{gr}	
39·1°	50	22·00	22·99	26·44	1·201
58·4°	50	21·05	22·02	25·27	1·200
76·5°	50	20·22	21·21	24·22	1·198
91·9°	50	19·75	20·64	23·65	1·197

α_{vi} could not be determined on account of the yellow colour of the fused substance.

d-β-Octyl p-nitro benzoate in alcoholic solution (approx. 5%)

Solvent.	gm. of ester in 100 cc. of solvent.	Temp.	Length of observation tube.	Rotations	α_{gr}/α_D	$[\alpha]$ Specific Rotations	$[M]$ Molecular Rotations
Alcohol	5·0652	22·3°	2 dcm.	α_D = 4·36 α_{ye} = 4·60 α_{gr} = 5·19 α_{vi} = 9·38	1·190	43·04 45·41 51·23 92·59	120·2 126·8 143·0 258·5

Drude Equation applied to the above rotations.

Rotations.	Drude Equation (one term) K	λ_o^2	α (calculated)	Differences. α(obs) - α (calc)
α_D = 4·36 α_{ye} = 4·60 α_{gr} = 5·19 α_{vi} = 9·38	1·282	·0532	α_D = 4·36 α_{ye} = 4·56 α_{gr} = 5·23 α_{vi} = 9·38	± ·00 + ·04 − ·04 ± ·00

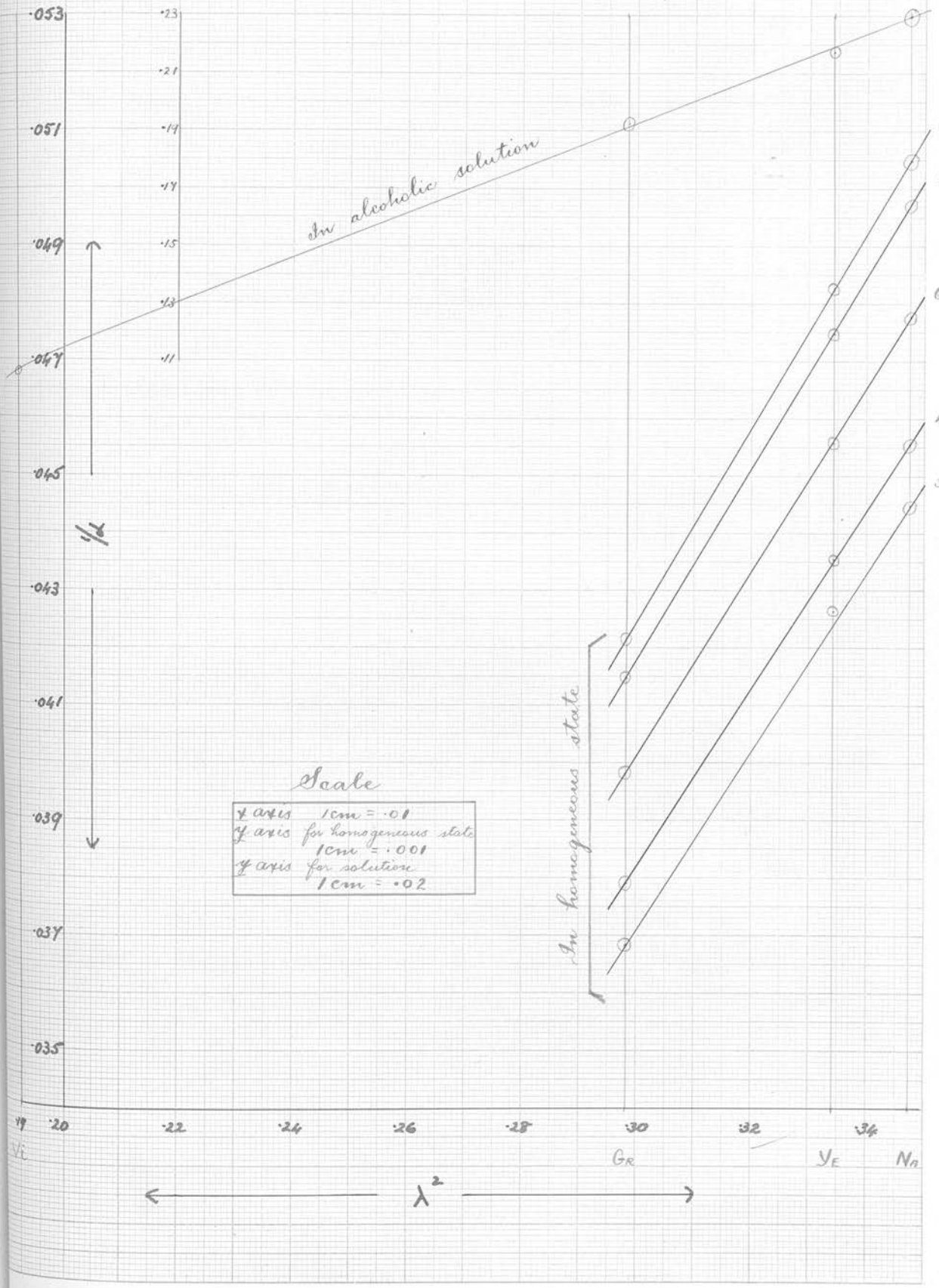
d - β - Octyl p - nitro benzoate.

Table showing densities, rotations, specific rotations and molecular rotations:

Temp.	Density	α_D	α_{ye}	α_{gr}	$[\alpha]_D$	$[\alpha]_{ye}$	$[\alpha]_{gr}$	$[M]_D$	$[M]_{ye}$	$[M]_{gr}$
30°	1·0655	22·48	23·46	27·14	42·20	44·04	50·94	117·8	123·0	142·2
40°	1·0573	21·95	22·96	26·37	41·52	43·43	49·88	115·9	121·3	139·3
60°	1·0410	20·93	21·94	25·11	40·21	42·15	48·24	112·3	117·7	134·7
80°	1·0249	20·11	21·07	24·11	39·24	41·12	47·05	109·6	114·8	131·4
90°	1·0168	19·81	20·72	23·73	38·97	40·75	46·68	108·8	113·8	130·3

d-β-Octyl p-nitro benzoate.

Graph showing $1/\alpha$ against λ^2.



Discussion of Results:

Before discussing the results given in the foregoing pages, it is necessary to summarise the rotations and dispersion ratios observed for the different compounds. In table I will be found the molecular rotations $[M]_D^{20^\circ}$ at 20°, 40°, 60°, 80° and 90°, together with the corresponding values for α_{gr}/α_D. and certain values for the nitro-benzoic esters in ethyl alcoholic solution.

I. Molecular Rotations and Dispersion Ratios of the Homogeneous Esters.

d-β-Octyl Methoxybenzoates.

Temp.	o-compound $[M]_D^{20^\circ}$	α_{gr}/α_D	m-compound $[M]_D^{20^\circ}$	α_{gr}/α_D	p-compound $[M]_D^{20^\circ}$	α_{gr}/α_D
20°	+33·27	1·131	+93·75	1·193	+113·3	1·199
40°	37·31	1·151	92·77	1·193	112·2	1·199
60°	40·82	1·163	91·61	1·194	111·0	1·198
80°	44·00	1·168	90·42	1·196	110·0	1·196
90°	45·38	1·169	89·82	1·196	109·4	1·196

d-β-Octyl Nitrobenzoates.

Temp.	o-compound $[M]_D^{20°}$	α_{gr}/α_D	m-compound $[M]_D^{20°}$	α_{gr}/α_D	p-compound $[M]_D^{20°}$	α_{gr}/α_D
20°	+121·6	1·244	+107·8	1·198	(30°)117·8	1·207
40°	119·6	1·237	104·2	1·195	115·9	1·201
60°	117·6	1·234	101·0	1·193	112·3	1·199
80°	116·1	1·234	98·2	1·194	109·6	1·199
90°	115·4	1·235	97·0	1·196	108·8	1·198

Note. For d-β-Octyl benzoate, Pickard and Kenyon (J.C.S. 1915, 107, 122) find $[M]_D^{20} = +77·84°$

Rotations of Nitrobenzoic esters in 5% Alcoholic Solution (at about 20°).

o-compound		m-compound		p-compound	
$[M]_D^{20}$	α_{gr}/α_D	$[M]_D^{20}$	α_{gr}/α_D	$[M]_D^{20}$	α_{gr}/α_D
155·8	1·338	103·1	1·187	120·2	1·190

For convenience of comparison the values obtained for the octyl chloro-benzoates (Rule & Paterson, to be published shortly) are also quoted.

Molecular Rotations and Dispersion Ratios of the chlorobenzoic esters. (at 20°).

o-compound		m-compound		p-compound	
$[M]_D^{20}$	α_{gr}/α_D	$[M]_D^{20}$	α_{gr}/α_D	$[M]_D^{20}$	α_{gr}/α_D
47·06	1·187	92·02	1·191	103·9	1·196

With these compounds may be included octyl hydrogen phthalate, the rotation value of which is greatly affected by variations in the solvent, concentration and temperature. Rule & Paterson have found that the normal rotation of this ester at 20° approximates to ± 117°.

Dispersion.

On plotting the reciprocal of the rotation against the square of the wave length, a straight line was obtained for the m- and p- methoxy derivatives (see p. 27 and p. 35). It may therefore be concluded that the dispersion of these substances under the con-

ditions of experiment is normal and apparently simple. The o-methoxy ester exhibits complex dispersion which is especially marked at the lower temperatures employed. The dispersions of the nitro-compounds in the homogeneous state are also complex, although the graphs of $1/\alpha$ against λ^2 for the m- and p- isomers in alcoholic solution approximate very closely to straight lines.

Over the range of temperature employed, the dispersion ratios α_{gr}/α_D for the m- and p- methoxy and nitro esters vary between 1·193 and 1·201 for the homogeneous compounds, if we except the higher value of 1·207 obtained for the p- compound in the neighbourhood of its melting point. They are thus of the same order as those found by Pickard & Kenyon (J.C.S. 1915, 107, 52) for the corresponding menthyl esters. The o-compounds are both abnormal in this respect. For octyl o-methoxy benzoate the ratio is 1·131 and rises rapidly with increase of temperature. The homogeneous o-nitro benzoate gives a ratio of 1·244 at 20°, which tends to drop with increase of temperature, but rises to 1·338 in alcoholic solution. The o- m- and p- chlorobenzoic esters of octyl alcohol exhibit normal and simple dispersion (Rule & Paterson unpublished results).

Influence of Substituents.

As may be seen from the above figures, the introduction of a methoxy group into the o-position in the benzene nucleus leads to a marked depression in the rotatory power of octyl benzoate, whereas a nitro group in the same position leads to a considerable increase. These conclusions may be compared with the results obtained by other workers. o-Substitution by a carboxyl group produces an increase, and by a chloro group a decrease in rotatory power (Rule & Paterson, unpublished) although in both cases the changes are smaller in magnitude than those due to the presence of a nitro or methoxy group in the o- position. The order and magnitude of the different rotations are shown by the following series:-

NO_2	>	COOH	>	H	>	Cl	>	OCH_3
121·6		117 (approx)		77·84		47·06		33·27

As in the case of menthyl benzoate therefore, the o-, p- directive groups produce a depression and the m- directive groups an exaltation of rotatory power. The rotations of the menthyl esters of α-

and β- naphthoic acids are depressed in a similar manner by the introduction of a methoxy group in the o- position to the carboxylic complex (compare Cohen and Dudley, J.C.S. 1910, 1748).

The above series corresponds exactly to that obtained by considering the values for the corresponding menthyl esters, viz:

$$NO_2 > COOH > H > Cl > OCH_3$$
$$-381 \quad -332 \quad -239 \quad -195 \quad -148$$

and the relative influence of these groups on benzene substitution is also given by the same series (Rule & Paterson, J.C.S. 1924, 125, 2156).

In the m- and p- positions the nitro, methoxy and chloro substituents all bring about a decided rise in the rotatory power of the octyl ester, thus contrasting strongly with their behaviour in the menthyl compound, in which the effect of m- and p- substituents is in most cases negligible.

The values for o-, m- and p- derivatives are not in complete agreement with Frankland's lever arm hypothesis, according to which the observed sequence should be p- > m- > H > o-. Although this expresses the results quoted for the methoxy and chloro deriv-

atives, it fails with the nitro and carboxy compounds, in which cases the o- derivative has a higher rotation than the unsubstituted ester.

Similarly the figures are not in agreement with the electrostatic modification of Frankland's hypothesis advanced by Rule (J.C.S. 1924, 1121), nor with the general conclusion arrived at by Cohen (loc.cit) from his study of the menthyl benzoates. This conclusion is that the element or group lying nearest to the active group produces the greatest effect, which, according to the nature of the group; may be an increase or decrease in rotation value, and that the rotation approaches the normal for the unsubstituted compound the farther the substituent is removed from its proximity to the active group.

It might be expected that the close relationship existing in certain cases between the influence of substituents on optical activity and acidity (Betti, Gazzetta, 1923, 53, 417; Rule & Smith, loc.cit.), would also be observed in the octyl benzoates, particularly among the m- and p- derivatives, in which the strong specific effect of the o- group is absent.

A comparison of the rotatory powers of the esters with the dissociation constants of the corresponding nitro, chloro and methoxy benzoic acids (quoted below)

	o-	m-	p-	
NO_2	0·62	0·035	0·040	
Cl	0·13	0·015	0·0093	(Benzoic acid k = 0·0068)
OCH_3	0·0082	-----	0·0033	

shows that the powerfully acidic nitro group affects rotatory and acidic strength qualitatively in the same manner, viz.

$$o\text{-}NO_2 > p\text{-}NO_2 > m\text{-}NO_2 > H$$

although for the resemblance to be complete the rotation of the o-nitro ester should be much higher than that found. The relatively high rotation of the o-isomeride is much more pronounced in alcoholic solution, especially when the values for $[M]_{vi}$ are compared. This agreement, however, does not hold in the case of the chloro and methoxy esters. The chloro group, which has a smaller acidic effect than the nitro group, gives the following order for rotations p - Cl > m-Cl > H > o-Cl, while the order of the dissociation constants is o-Cl > m-Cl > p-Cl > H. The sequence given by the weakly acidic methoxy

group is p-OCH_3 > m-OCH_3 > H > o-OCH_3 for the rotatory power and o-OCH_3 > H > p-OCH_3 for acidic strength.

It is curious that in the p- position the otherwise dissimilar nitro, chloro and methoxy groups produce the same pronounced increase in rotation.

In general the molecular rotations of the octyl esters fall with rise of temperature, as may be seen from the figures given in table I. An exception is found in the o-methoxy ester, the rotation of which increases with rise of temperature.

Summary.

The investigation of a number of optically active octyl esters of o-, m-, and p- substituted benzoic acids reveals a regularity in the influence of substituents in the ortho-position.

The m-directive or positive nitro and carboxyl groups increase the rotation of octyl benzoate, whereas the o- and p- directive or negative methoxy and chloro groups decrease the rotation. Further, the relative influence of these groups with respect to hydrogen is in agreement with their relative influence

on the rotation of menthyl benzoate and with their relative influence on the substitution of benzene.

The writer wishes to acknowledge her indebtedness to Dr H. G. Rule for his helpful suggestions and advice during the course of this work.